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ICPMS as an element-specific detector for the analysis of trace element species and nanoparticles

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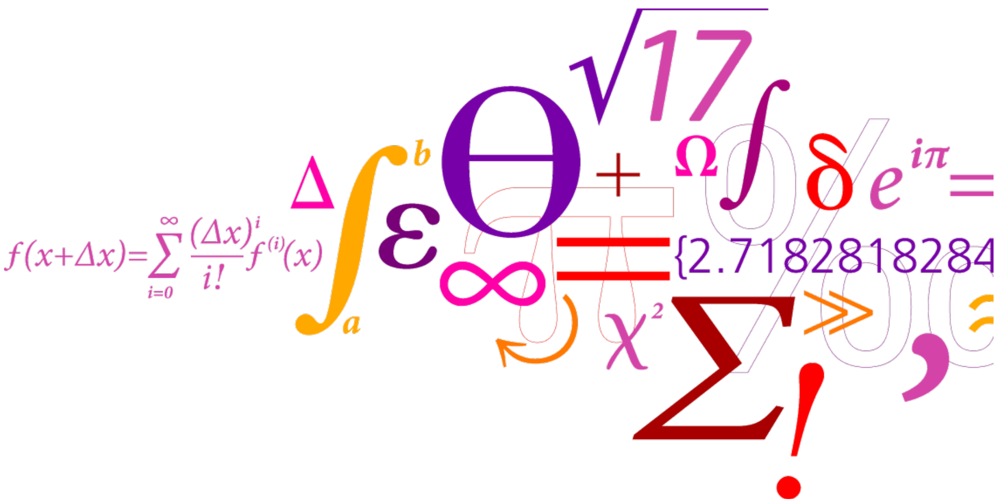
ICPMS as an element-specific detector for the analysis of trace element species and nanoparticles

Jens J. Sloth

Xenia Trier, Katrin Loeschner and Erik H. Larsen



Inductively Coupled Plasma Mass Spectrometry

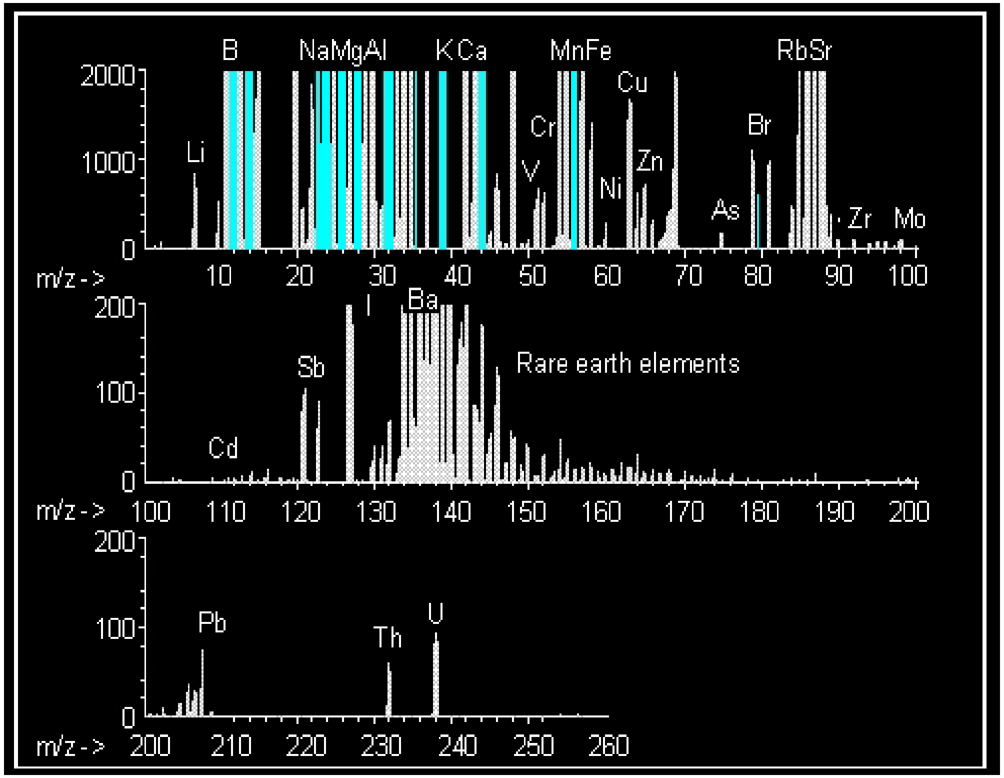
ICPMS

ICP-MS (Inductively coupled plasma mass spectrometry) is a type of mass spectrometry that is highly sensitive and capable of the determination of a range of metals and several non-metals at concentrations below one part in 10^{12} (ppt). It is based on coupling together an inductively coupled plasma as a method of producing ions (ionization) with a mass spectrometer as a method of separating and detecting the ions. ICP-MS is also capable of monitoring isotopic speciation for the ions of choice.

Keywords:
- High sensitivity
- Multielement analysis
- Isotopic speciation

Agilent ICPMS 7500ce

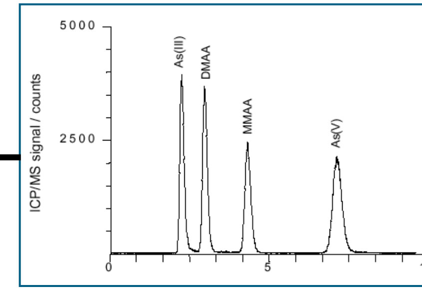
Mass spectrum – isotopic pattern of the elements



ICPMS working range is from 6-250 m/z
From lithium to uranium

Speciation analysis of elements

Workhorse: HPLC-ICPMS (or GC-ICPMS)



HPLC / GC

Sample introduction

Column

Separation

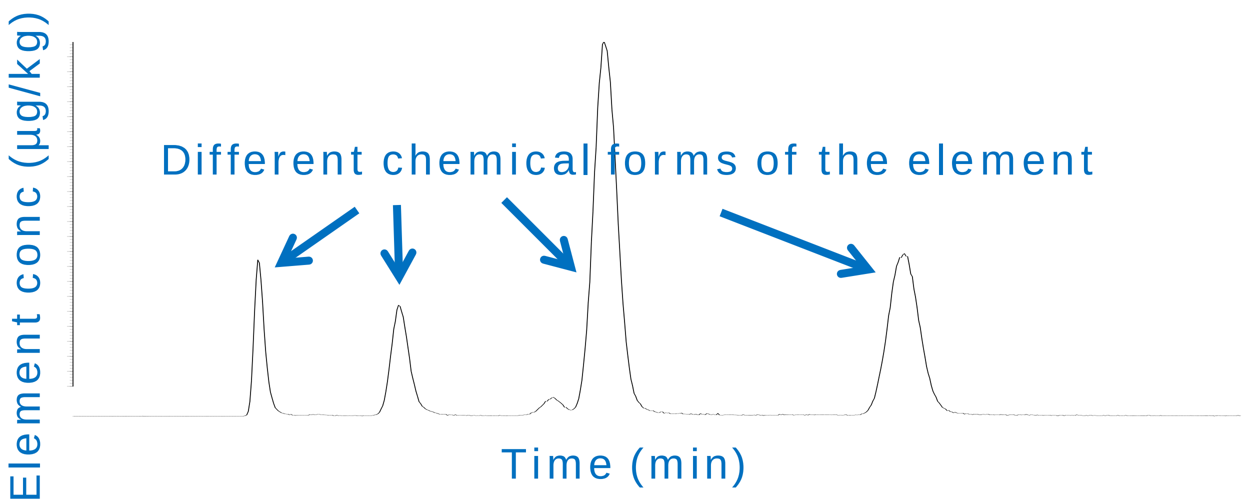
ICPMS

Element specific detection

Result

Chromatogram

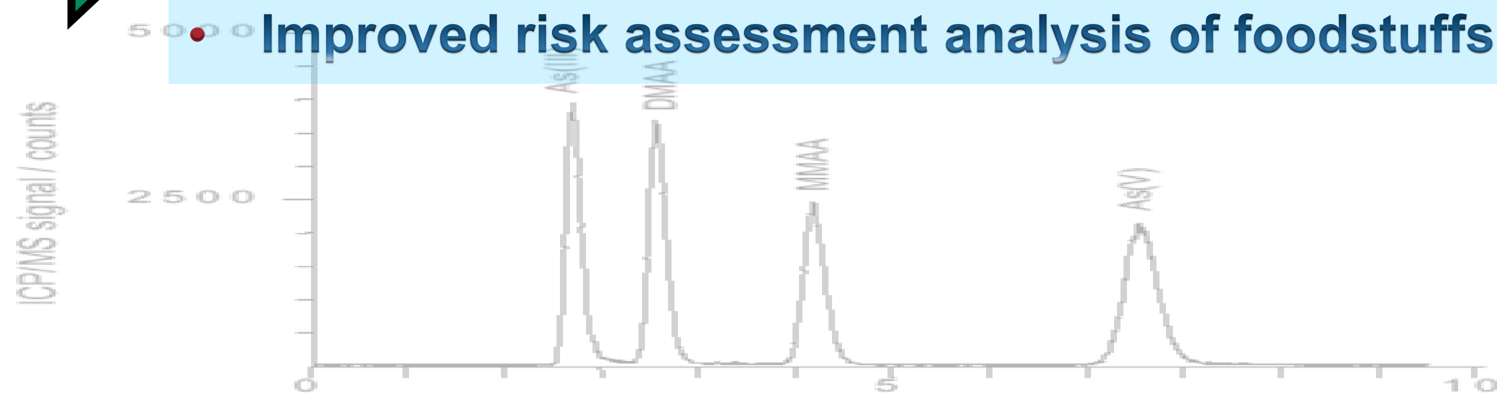
Output:
Element-specific chromatogram



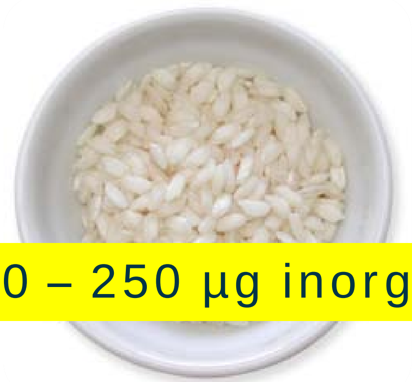
EXAMPLES

- **Arsenic** speciation analysis by HPLC-ICPMS
- **Organotin** speciation analysis by GC-ICPMS
- **Nanoparticle** determination by FFF-MALS-ICPMS

- Beyond total element determination
- Species-specific information
- Improved risk assessment analysis of foodstuffs



Example – arsenic speciation analysis
Important for correct risk assessment



~ 40 – 250 µg inorg As

<10 µg inorg As

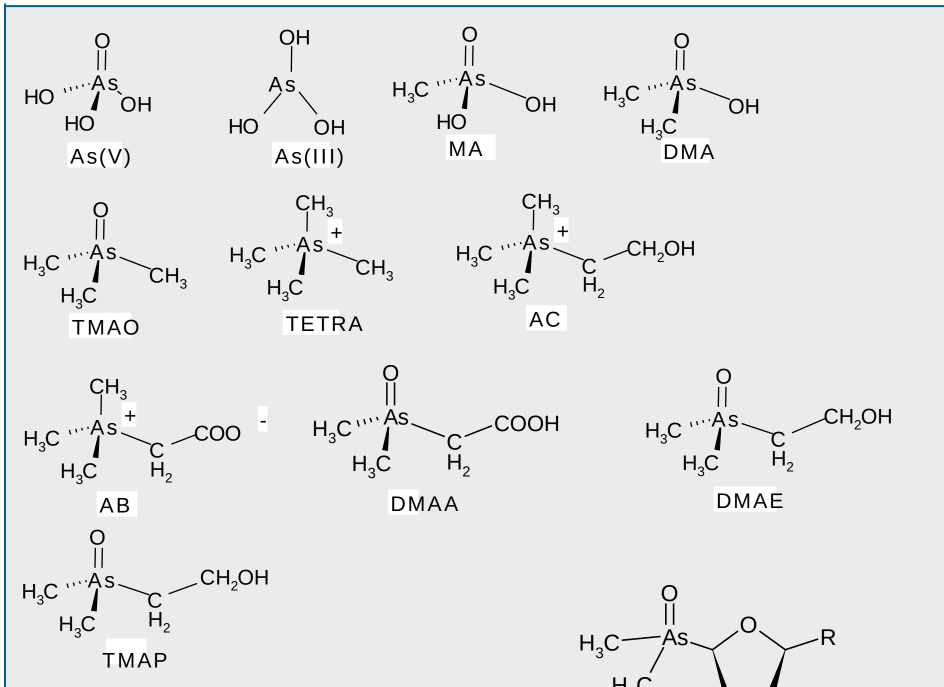
1 kg rice => 50-300 µg As

1 kg fish => 3000-10000 µg As

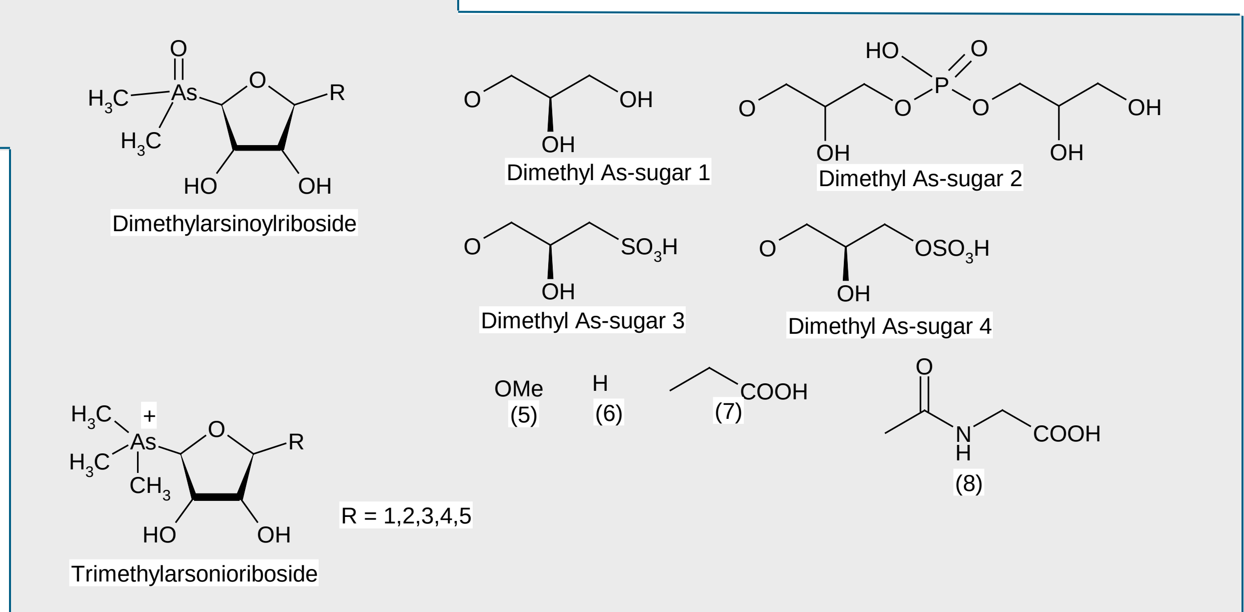
There is most focus on rice from a food safety point of view – why???

The chemical form of arsenic is important
=> Arsenic speciation

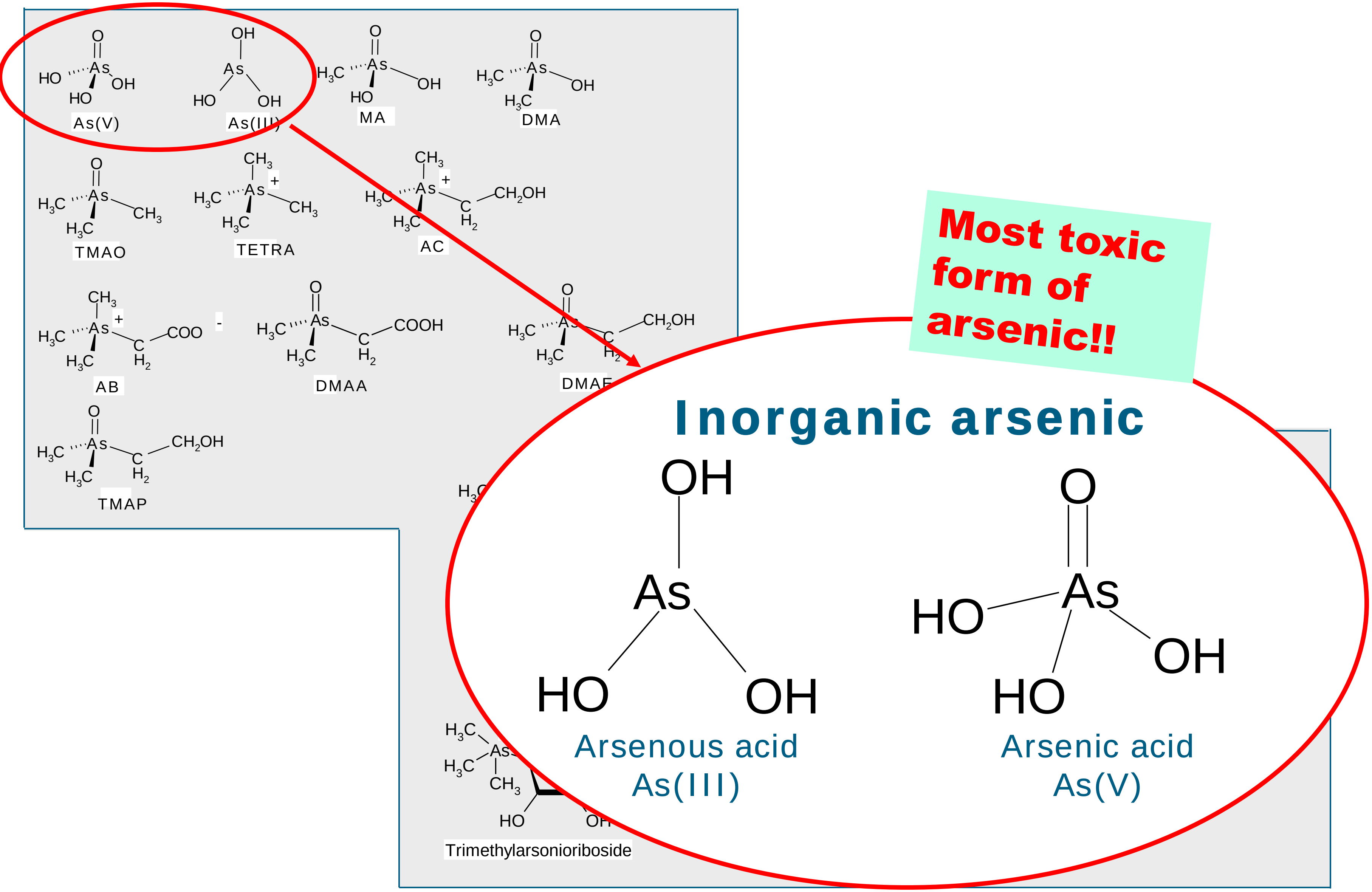
Arsenic compounds in the marine environment



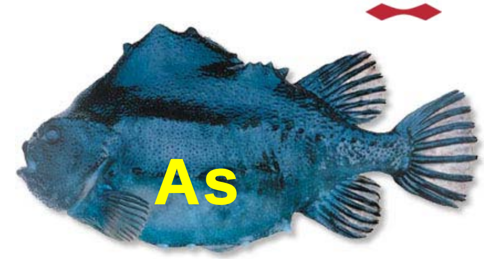
More than **50** different arsenic species have been found in the marine environment



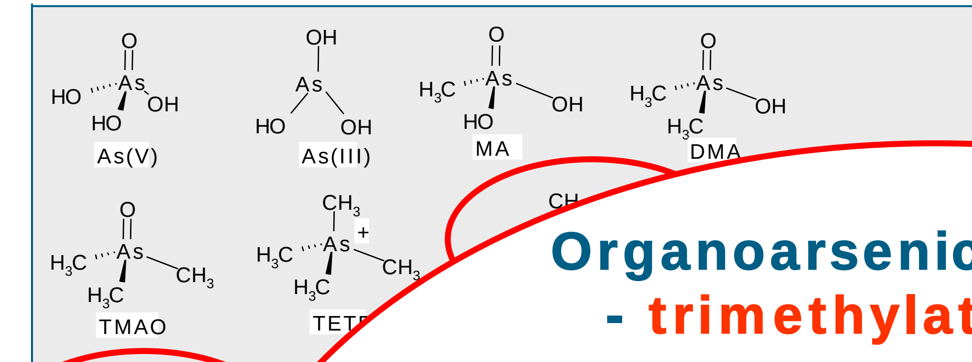
Arsenic compounds in the marine environment

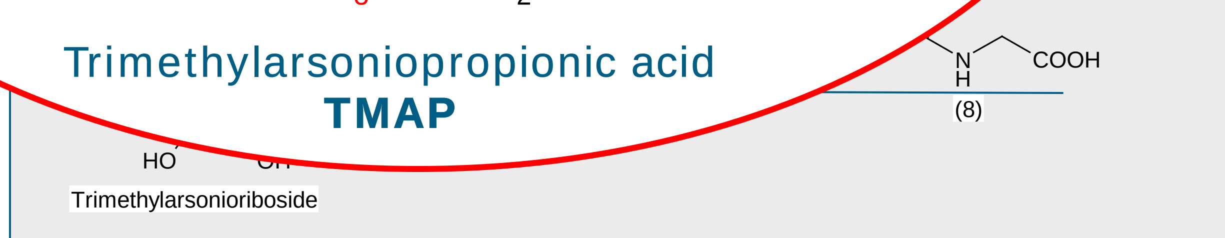


Arsenic compounds in the marine environment

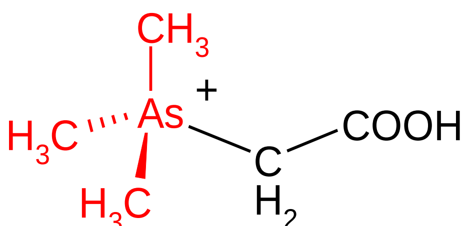


AB="fish arsenic"

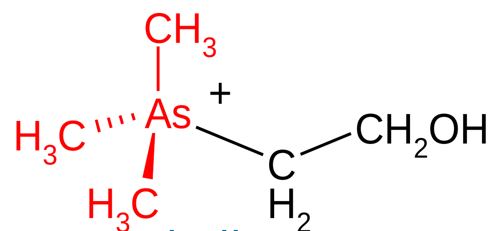




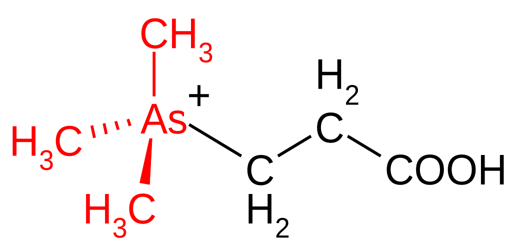
Organoarsenic compounds - trimethylated species



Arsenobetaine
AB



Arsenocholine
AC



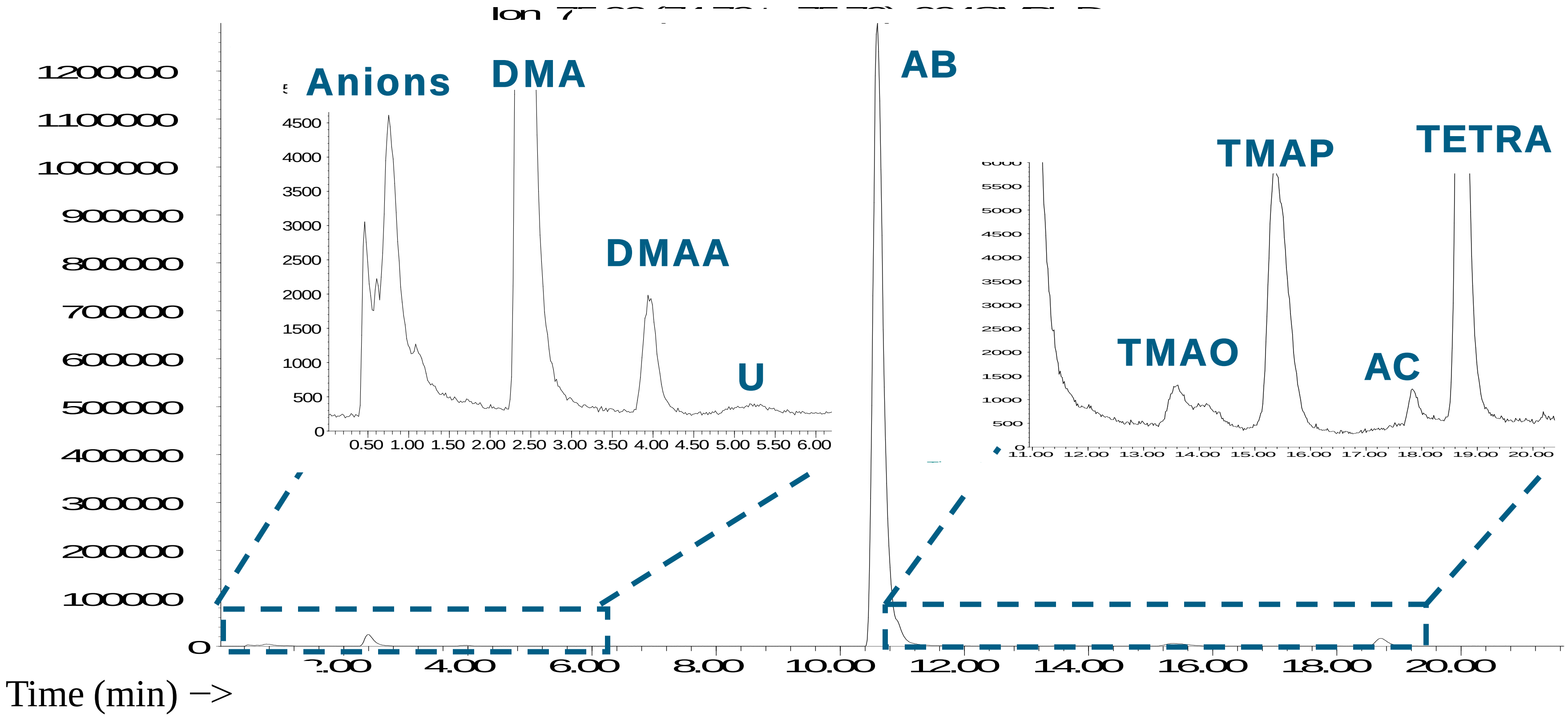
Trimethylarsoniopropionic acid
TMAP

Predominant form of arsenic in most seafood!!

Arsenic speciation in fish muscle by HPLC-ICPMS

Cation-exchange chromatogram of a MeOH/H_2O extract of CRM DORM-2

Column: Chrompack Ionospher 5C; Mobile phase: Pyridine; pH = 2.7

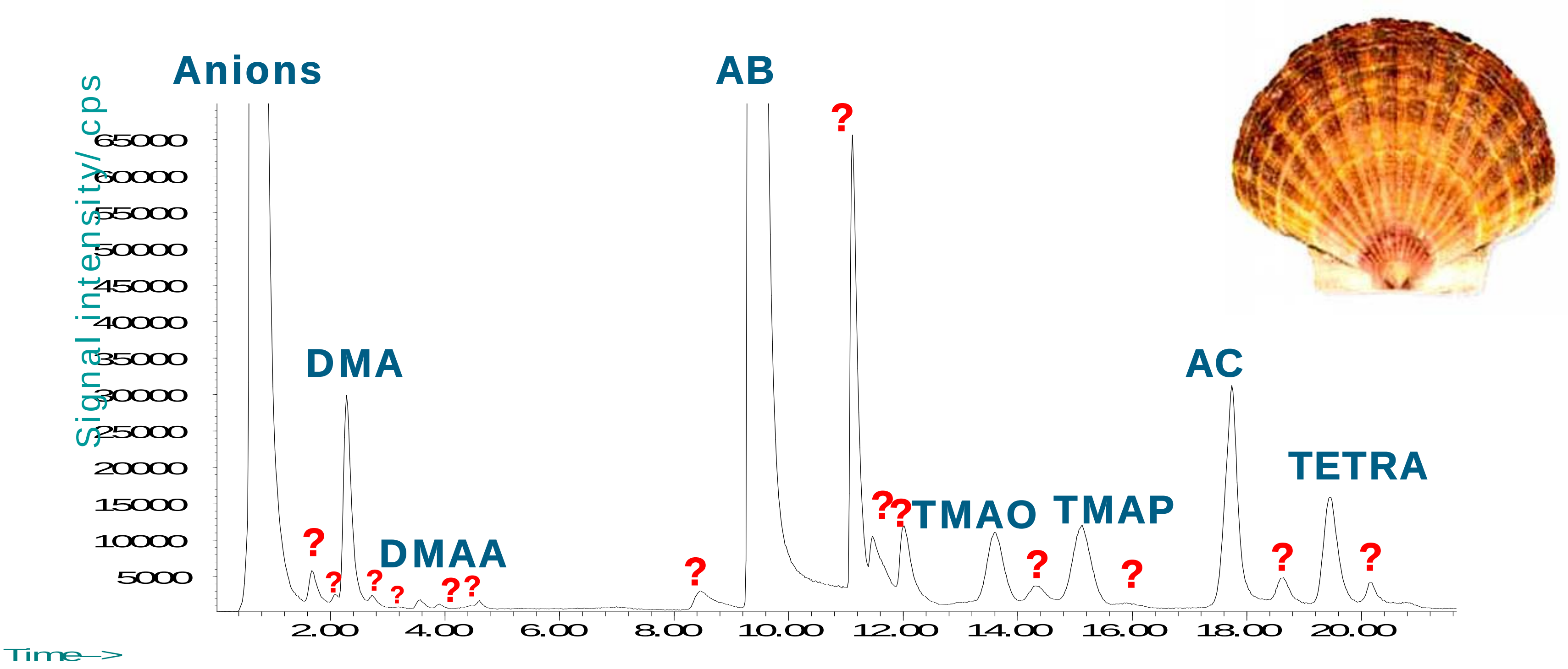


Sloth *et al*, J.Anal.Atom.Spectrom., 2003

Speciation analysis of arsenic of scallop kidney

Cation-exchange with gradient elution – extraction with aqueous methanol (50%)
Column: Chrompack Ionospher 5C; Mobile phase: Pyridine; pH = 2.7

- seven compounds identified by coelution with available standards
- **16** non-identified peaks



? = unknowns (limitation of ICPMS detection)

Sloth *et al*, J.Anal.Atom.Spectrom., 2003

EFSA (2009) and JECFA (2010) opinions on arsenic in food

=>Risk assessments of dietary arsenic exposure

FOCUS ON INORGANIC ARSENIC

European Food Safety Authority

- **NEW! BMDL$_{1.0}$ = 0.3 – 8 µg/kg bw per day for inorganic arsenic**
- *=> EU dietary exposures within this range for average and high level consumers*
- *=> Risk to some consumers cannot be excluded*

Food and Agriculture Organization of the United Nations

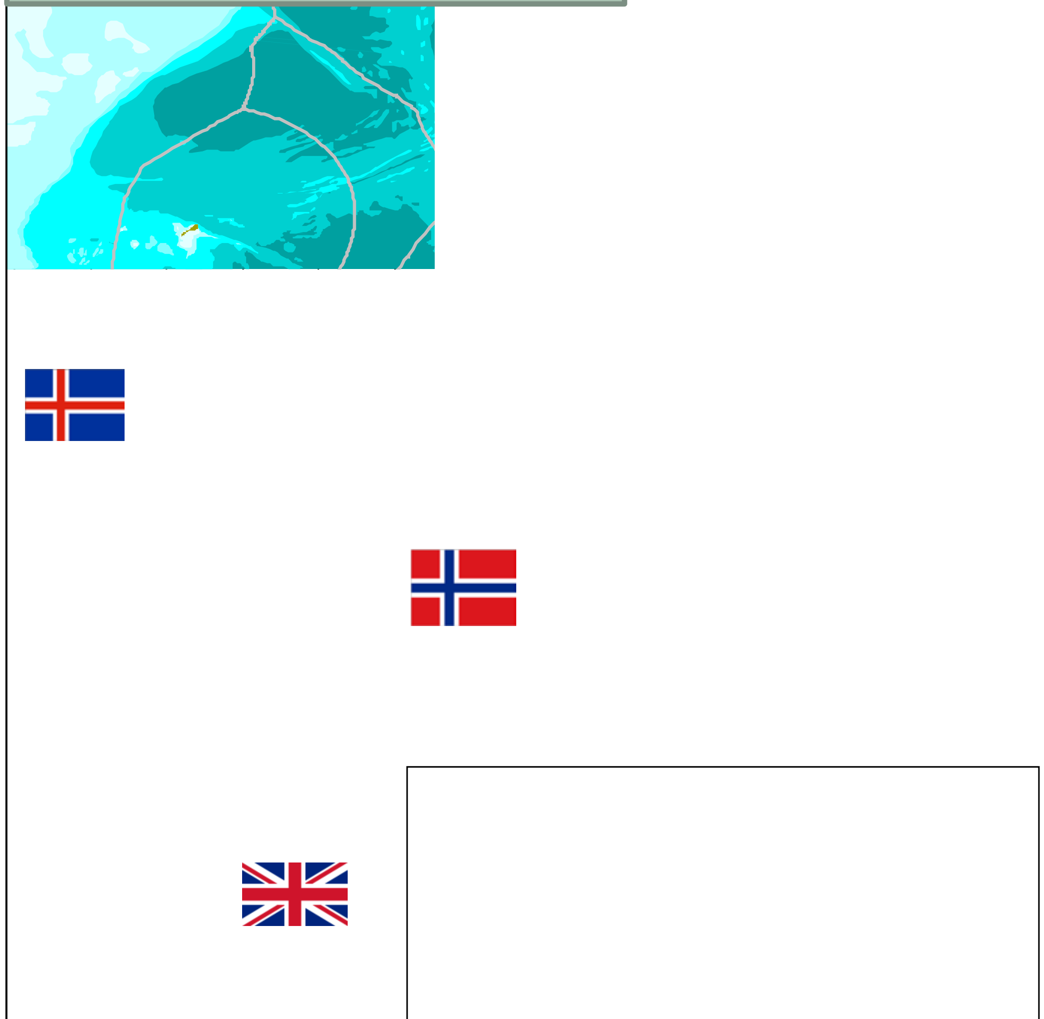
- **NEW! BMDL$_{0.5}$ = 3 µg/kg bw per day for inorganic arsenic**
- *=> 0.5% increased incidence of lung cancer for 12 y exposure*

"…there is a need to produce speciation data for different food commodities to support dietary exposure assessment…"

"…more accurate information on the inorganic arsenic content of foods is needed to improve assessments of dietary exposures to inorganic arsenic"

Inorganic arsenic in wild caught fish => no concern

iAs analysed by HPLC-ICPMS



Norwegian survey

900 individual fish samples

- Atlantic halibut
- Cod
- Greenland halibut
- Mackerel
- Herring
- Tusk

Results

Total arsenic……….0.3-110 mg/kg

Inorganic arsenic….< 0.01 mg/kg

(only 37 samples > LOQ)

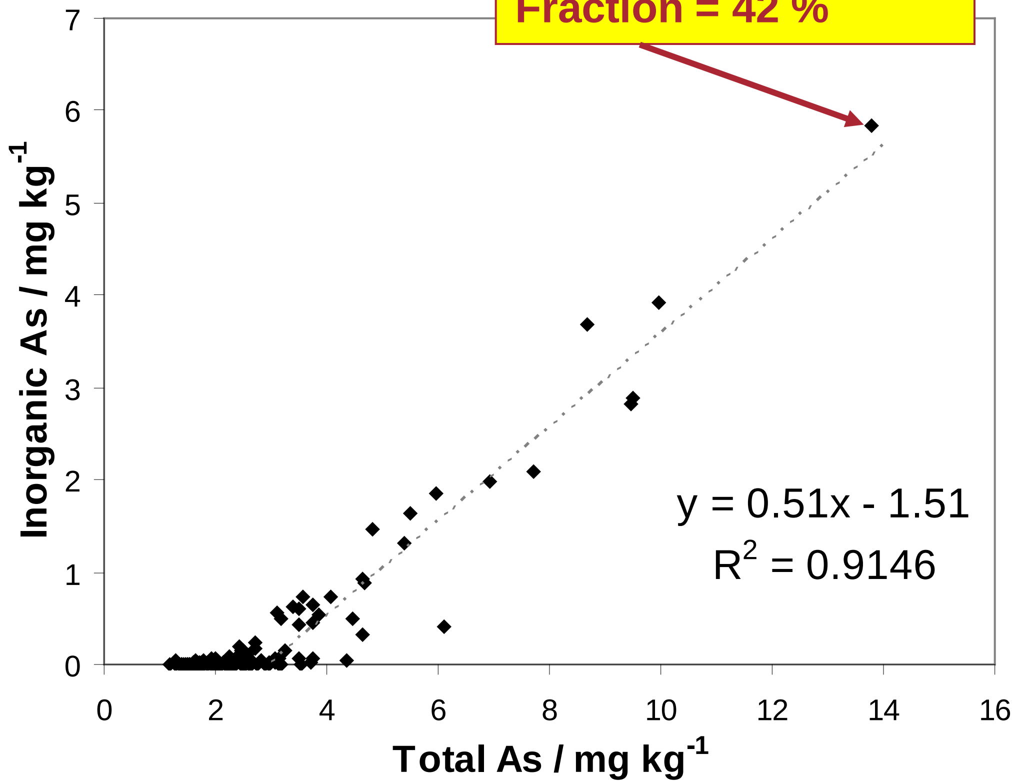
NIFES
NATIONAL INSTITUTE OF NUTRITION AND SEAFOOD RESEARCH

Julshamn and Sloth, 2012, Fd Addit Contam, submitted

...but in bivalves high contents in some samples...

iAs analysed by HPLC-ICPMS

Total As = 13.8 mg/kg
Inorg As = 5.8 mg/kg
Fraction = 42 %



Data from 175 blue mussel (*Mytilus edulis*) samples collected along the Norwegian Coastline.

NIFES
NATIONAL INSTITUTE OF NUTRITION AND SEAFOOD RESEARCH

Sloth and Julshamn, 2008, J. Agri.Food Chem., 56, 1269-1273

Arsenic in rice – an emerging health issue?

ER

Environmental Pollution 152 (2008) 746–749

Rapid communication

Inorganic arsenic levels in baby rice are of concern

Andrew A. Meharg [a,*], Guoxin Sun [b], Paul N. Williams [a,b], Eureka Adomako [a], Claire Deacon [a], Yong-Guan Zhu [b], Joerg Feldmann [c], Andrea Raab [c]

[a] School of Biological Sciences, University of Aberdeen, Cruickshank Building, St. Machar Drive, Aberdeen AB24 3UU, UK
[b] Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Median consumption of organic arsenic levels for UK babies from baby rice is above threshold considered safe.

- 17 samples from supermarkets in Aberdeen
- Total arsenic levels: 0.12 – 0.47 mg/kg
- Inorg
- 35%

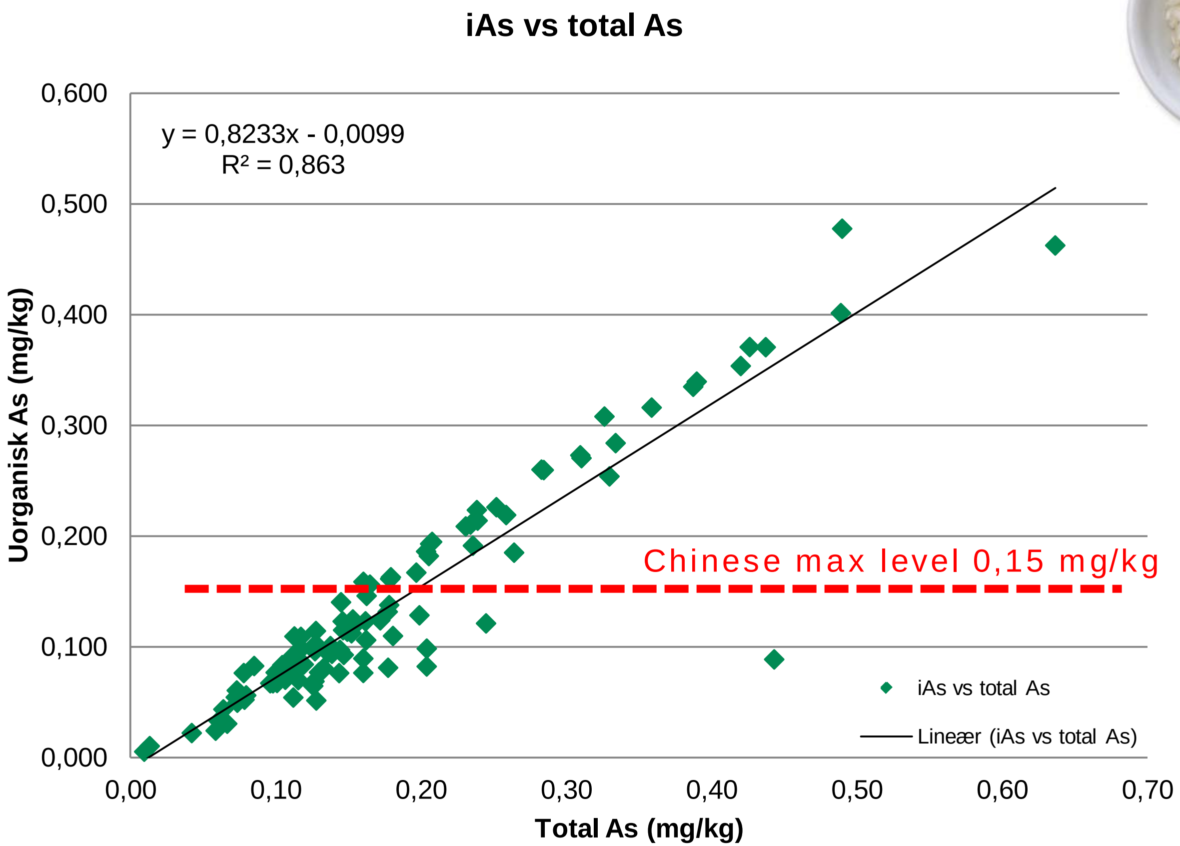
COMMUNICATION www.rsc.org/jem | Journal of Environmental Monitoring

Inorganic arsenic levels in rice milk exceed EU and US drinking water standards

Andrew A. Meharg,[a] Claire Deacon,[a] Robert C. J. Campbell,[a] Anne-Marie Carey,[a] Paul N. Williams,[a] Joerg Feldmann[b] and Andrea Raab[ab]

- 19 rice milk samples from supermarkets
- EU drinking water ML: 10 µg/L total As (100% of samples exceeded)
- US drinking water ML: 10 µg/L iAs (80% of samples exceeded)

Arsenic in rice products DK - survey



iAs analysed by HPLC-ICPMS

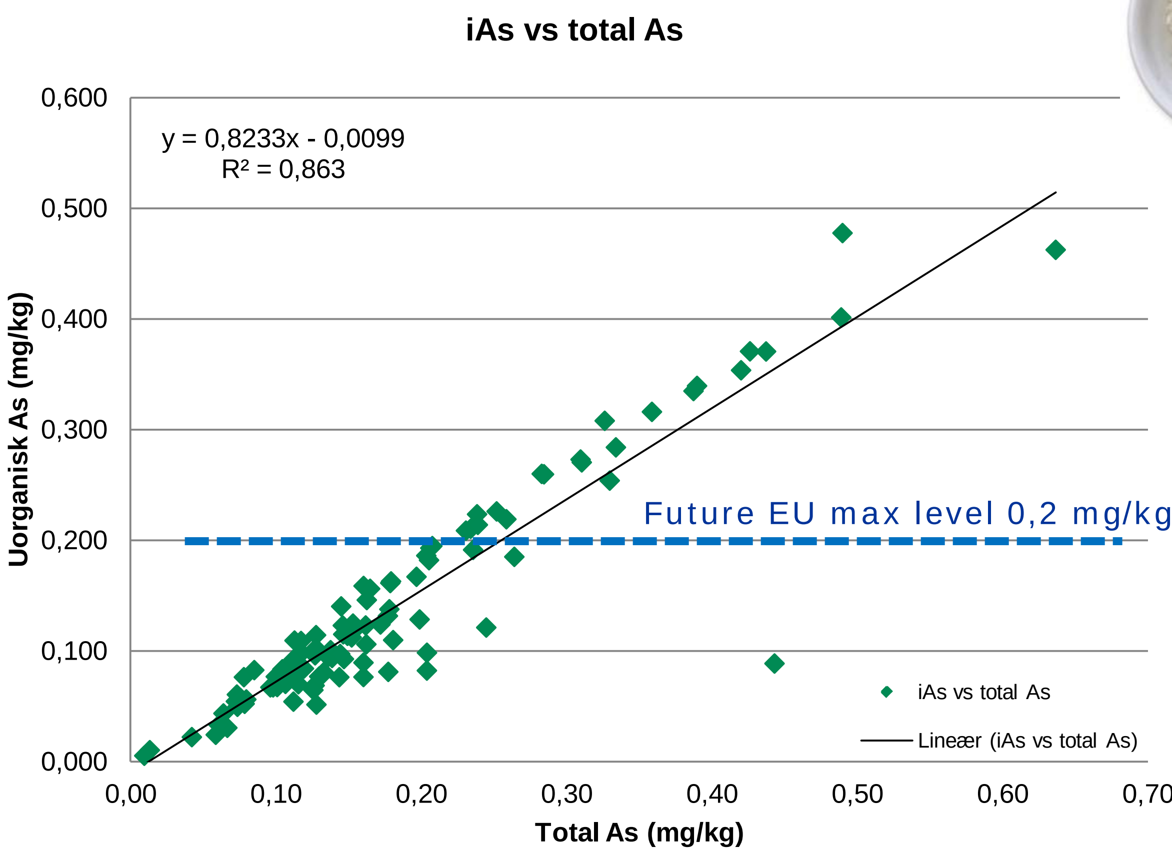
105 samples
- -white rice
- -brown rice
- -red rice
- -black rice
- -rice crackers

33 samples > 0,15 mg/kg
- -2 parboiled (20%)
- -4 brown (50%)
- -4 red (50%)
- -5 black (71%)
- -1 Basmati (10%)
- -1 Pudding rice (9%)
- -1 wild rice (20%)
- -15 rice crackers (100%)

Ministry of Food, Agriculture and Fisheries
Danish Veterinary and Food Administration

Sloth et al, in prep

Arsenic in rice products DK - survey



iAs analysed by HPLC-ICPMS

<u>105 samples</u>

-white rice
-brown rice
-red rice
-black rice
-rice crackers

<u>22 samples > 0,2 mg/kg</u>

-1 parboiled (10%)
-1 brown (12%)
-3 red (37%)
-2 black (28%)
-0 Basmati (0%)
-0 Pudding ri (0%)
-0 wild rice (
-15 rice crac

Rice cracker mean: 0.31 mg/kg – intake 50 g/dag => 15 µg iAs (~1 µg/kg b

> EFSA BMDL$_{01}$ 0.3-8 µg/kg bw/dag

Sloth et al, in prep

Inorganic arsenic in chinese food supplements

Name of Food supplement	Total Arsenic (µg/g)	Inorganic arsenic (µg/g)
Xiao Yao Wan	0.82	0.85
Bu Zhong Yi Qi Wan	0.62	0.50
Da Bu Yin Wan	0.59	0.55
Six Flavor teapills	0.72	N.D.
Golden Book Teapills	0.58	0.57
Xiang Sha Liu Jun Zi Wan	0.94	0.80
Gan Mao Ling	1.24	1.01
Chuan Xin Lian	5.00	3.17
Bi Yan Pian	0.70	0.58
Arouse power	1.12	1.02
Bio Chlorella	0.62	0.21
Unik Spirulina Kapsler	2.59	0.13
Chlorella	0.58	0.03
Ez-Biloba	0.63	0.67
Qvinde Dong Quai	0.68	0.48

Gan Mao Ling
(against flu and common cold)

Rec dose: 18 pills per day
⇒ iAs ~ 13 µg/day
⇒ 0.22 µg/kg bw/day (@60 kg)
Close to EFSA $BMDL_{01}$!!

iAs analysed by HPLC-ICPMS

Hedegaard and Sloth, in prep

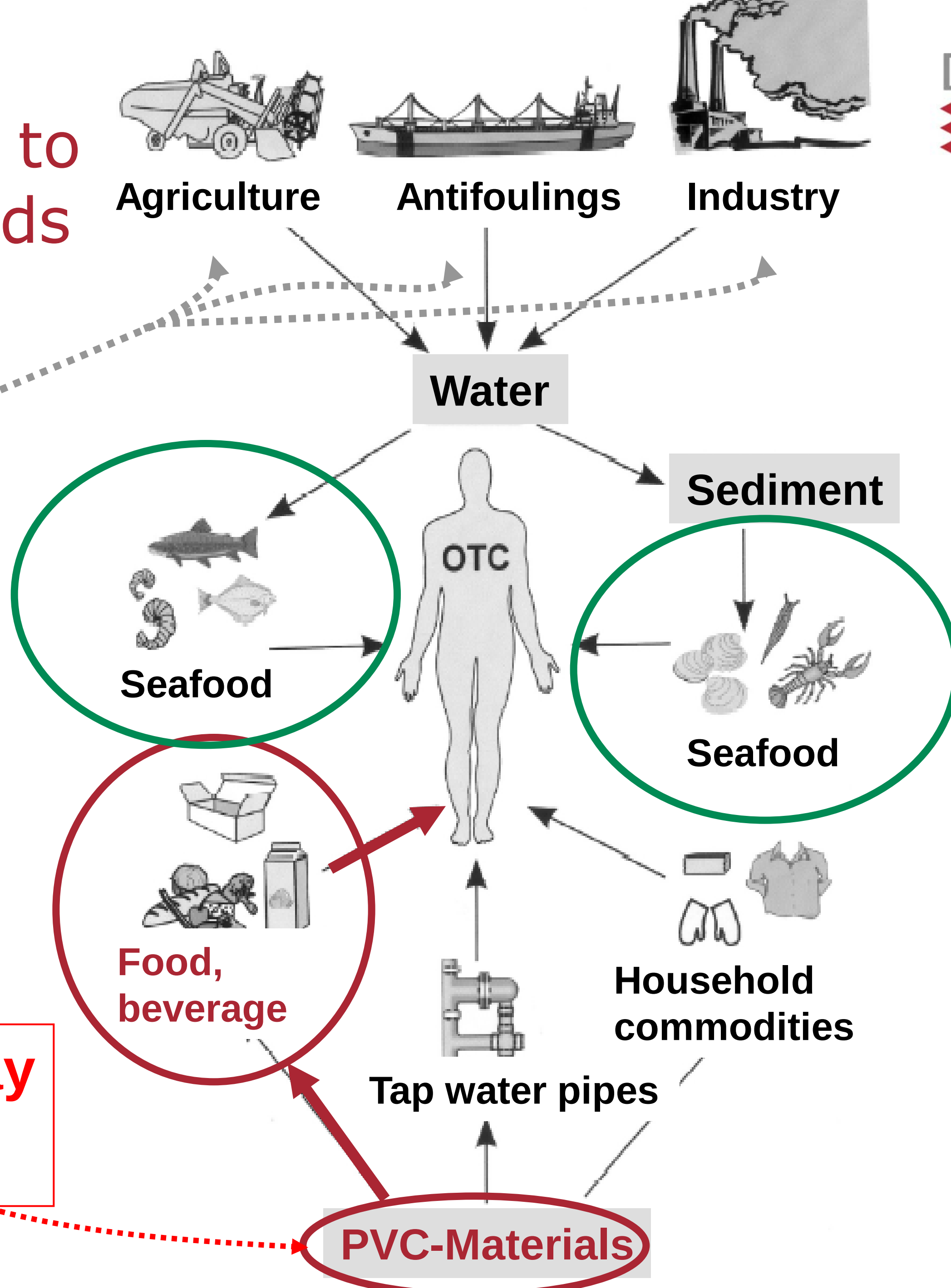
Routes of exposure to organotin compounds

Used in
- **Agriculture**
- **Antifoulings**
- **Industry**

- **PVC-Materials**

TDI: 0.25 µg/kg bw/day

∑TBT, DBT, TPhT and DOT



Hoch, Appl. Geochem., 2001, 719-43

Legislation on OTCs in Food Contact Materials

Compounds	Maximum level (µg Sn/kg foodstuff)
$\sum$ DBT, TBT, TPhT and DOT	40 (6)
$\sum$ MMT, DMT	180
MOT	1200
MDDT	12000 (50)
DDDT	24000 (50)

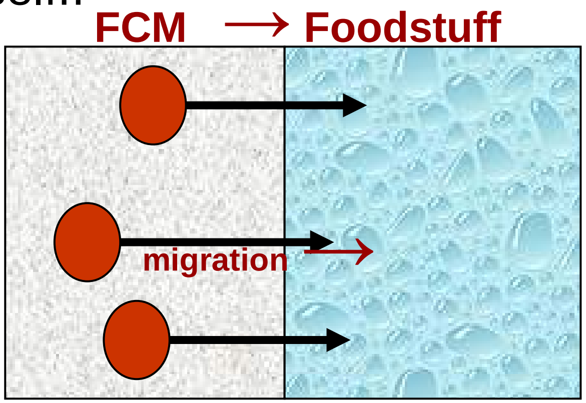
Ref: EFSA (2005); proposed EFSA values in parenthesis

Assumptions:

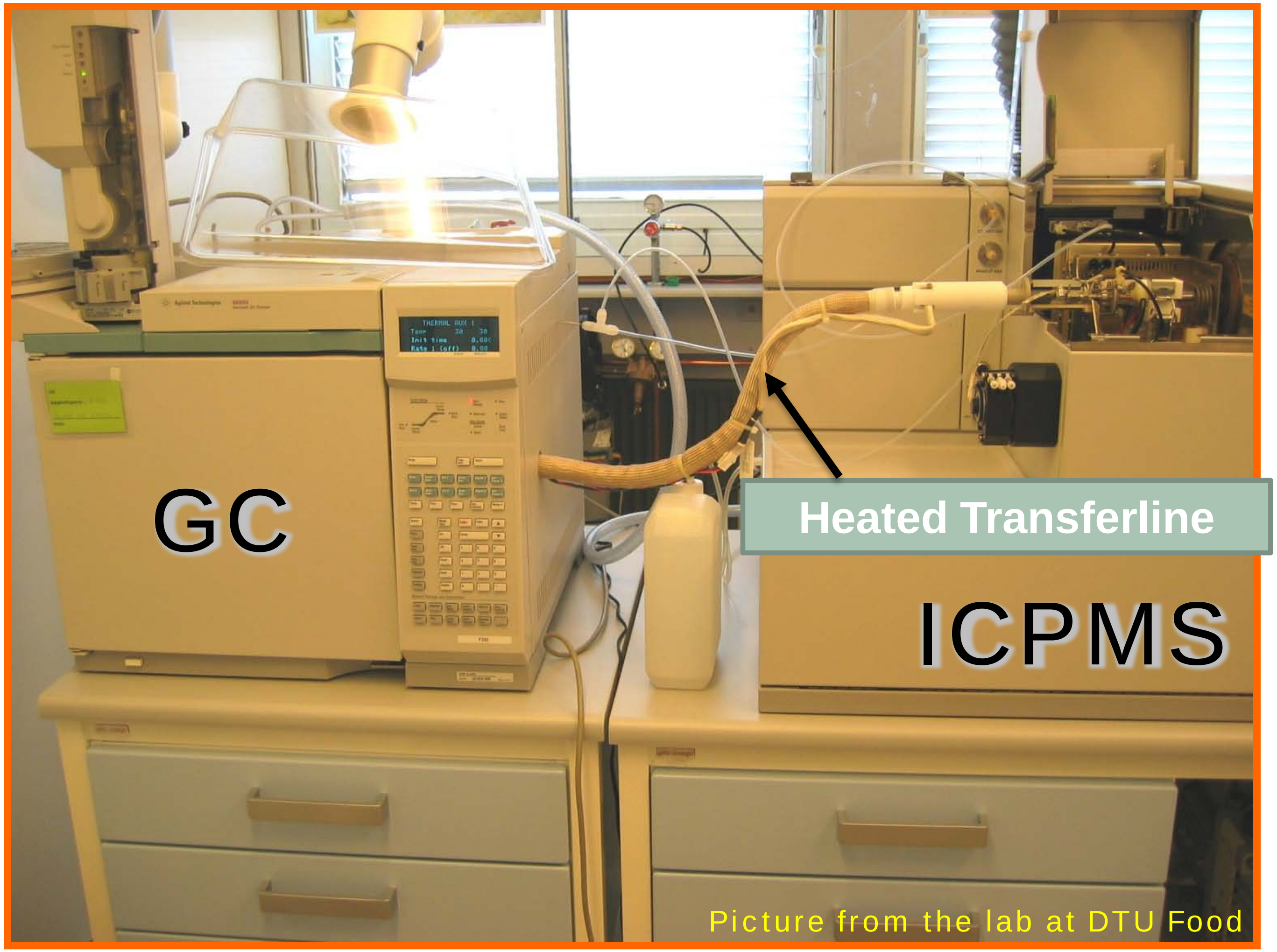
- 1 kg food per 6 dm^2

- 100 mL in contact with 0.6 dm^2

- Max levels on organotin migrating from the packaging material
- Testing by the use of food simulators (water, acid, oil, alcohol etc)
- BUT no maximum levels on organotins in the foodstuff itself!!



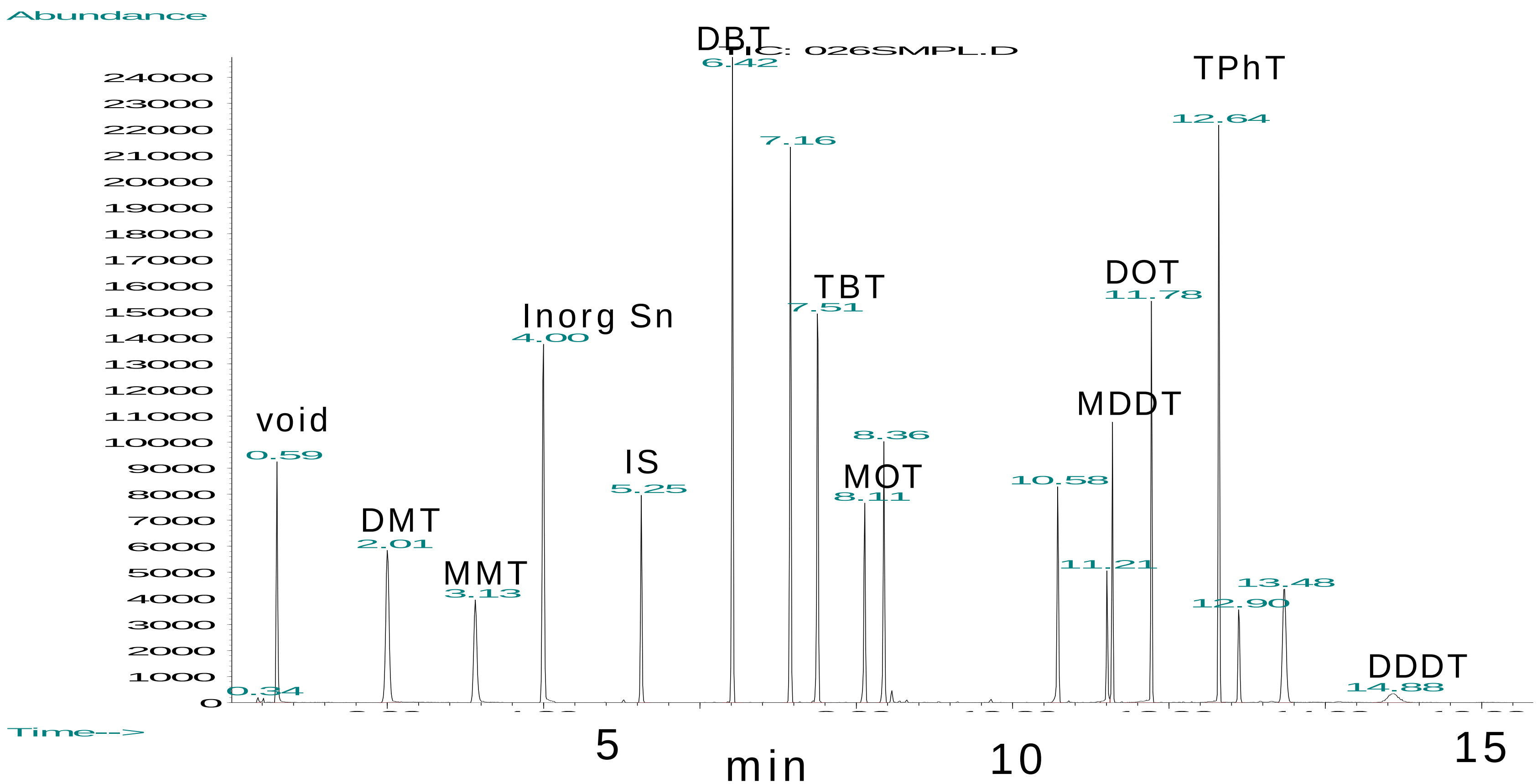
GC coupled to ICPMS



...can be used to determine organotin compounds

Organotin speciation by GC-ICPMS

- Chromatogram of 9 standards + IS



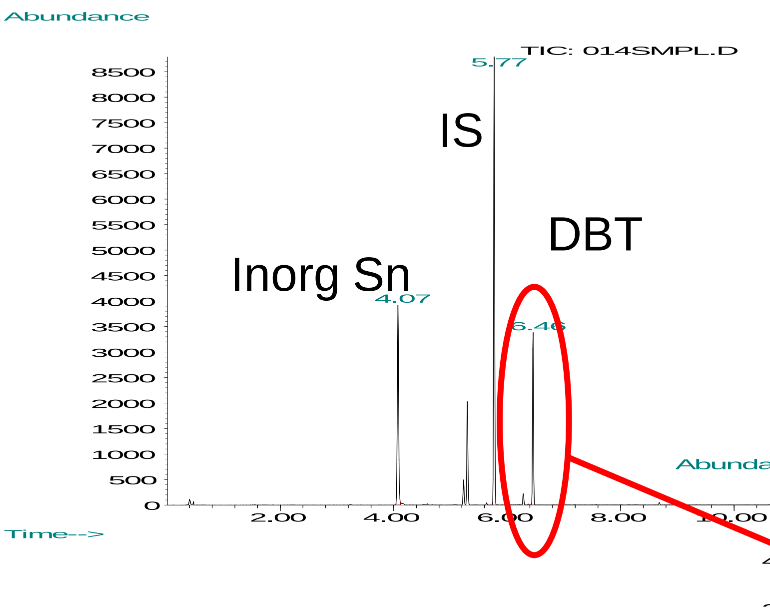
Derivatisation (ethylation) with $NaBEt_4$

Organotin migration from Food Contact Materials

Small scale survey on 33 Food Contact Materials

Baking paper, PVC cling films, silicone baking forms, lids with PVC gaskets

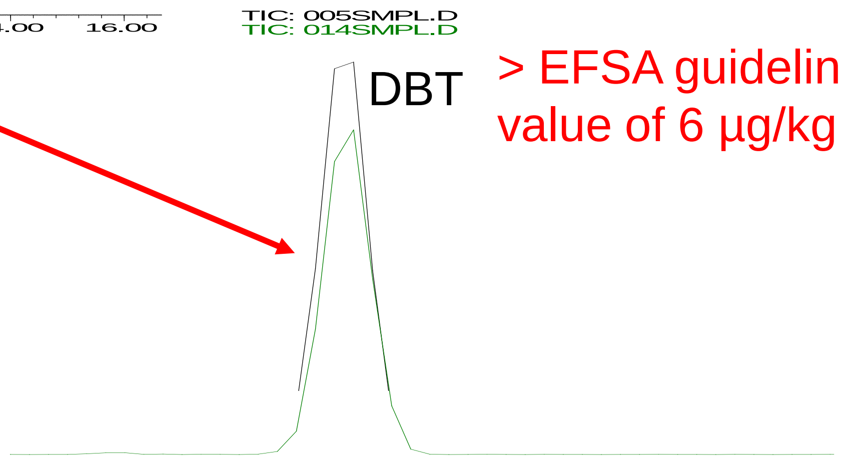
PUR-agglomerated cork wine stoppers



- PVC lid
- 3% acetic acid

Overlaid standard and sample

- DBT concentration: 9.9 µg/kg



> EFSA guideline value of 6 µg/kg

Output of DK survey:
-33 samples
-11 contained OT (mainly DBT)
-3 exceeded EFSA guideline limit

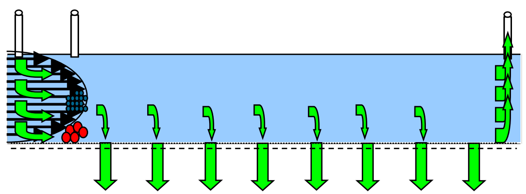
Sloth&Trier et al, in prep

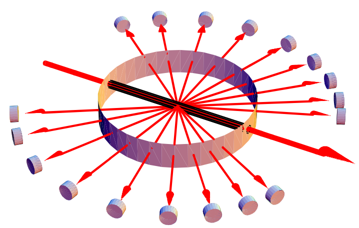
Silver nanoparticles in products related to food and beverages

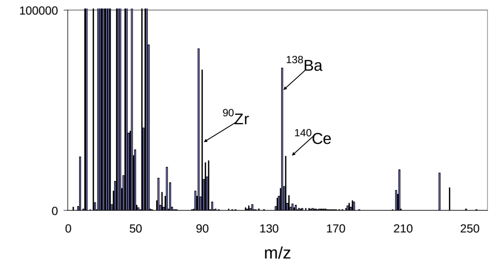
http://www.nanotechproject.org/

The analytical platform

AF^4 – MALS - ICPMS







Asymmetric flow field flow fractionation

Optical detection (multi angle and dynamic light scattering, UV and fluorescence)

Inductively coupled plasma mass spectrometry (ICP-MS)

Particle separation according to their size (small NPs elute first)

Particle detection (fractogram)

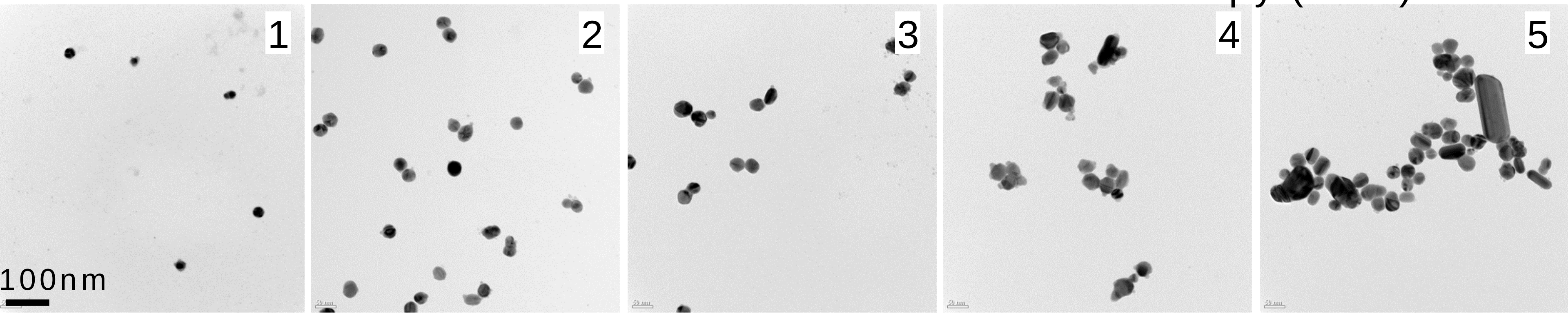
Size determination

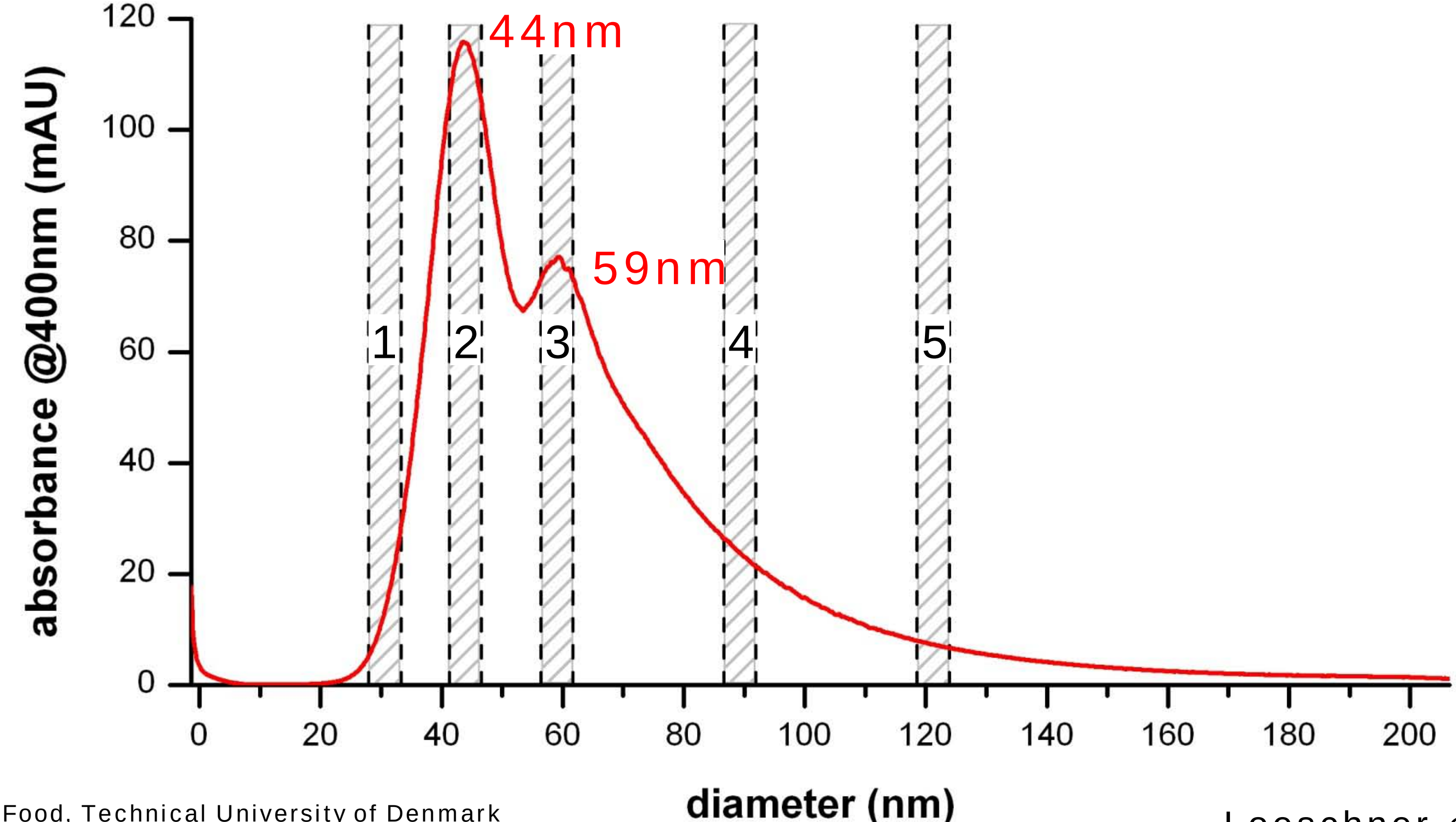
Elemental detection for ID of the particles

Quantification

Determination of Ag-nanoparticle size distribution

Fraction collection for transmission electron microscopy (TEM)





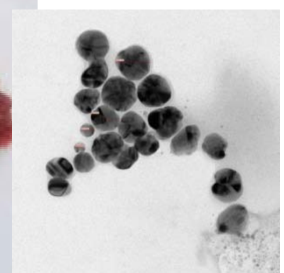
Loeschner *et al*, in prep

NanoLyse Project

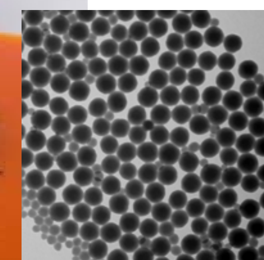
"Nanoparticles in Food: Analytical methods for detection and characterisation"

Validated methods for the determination of inorganic ENP in food extracts, based on size separation, size determination and specific detection

silver nanoparticles in lean meat



silica nanoparticles in tomato soup



http://www.nanolyse.eu

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Kåre Julshamn

DTU Food National Food Institute

Ministry of Food, Agriculture and Fisheries
Danish Veterinary and Food Administration

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Danish Food Administration (DFVA)

Norwegian Food Authority

NANOLYSE

Ministry of Food, Agriculture and Fisheries
Danish Veterinary and Food Administration

Mattilsynet

Thanks for your attention!